Structure and Properties of Dental Resin Composites containing Tricalcium Phosphate and Hydroxyapatite Fillers

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Abstract

Objective: The purpose of this study was to correlate the structure of beta Tricalcium phosphate (β-TCP) and hydroxyapatite (HAP) with the key properties of the experimental resin composites.

Methods: β-TCP and three types of HAP powders labelled as A, B and C were examined under SEM to study their morphology. The particle size was measured using a laser diffraction particle size analyser. These fillers were used to prepare the experimental resin composites. The matrix was composed of a visible light-cured monomer urethane dimethacrylate (UDMA). Five resin composites from each type of filler were prepared by varying filler loading ratio from 20 to 60 % by weight.

The properties studied for each resin composite were Vickers hardness, Surface gloss and Surface roughness. Vickers hardness (VHN) was evaluated immediately and after dry storage at 37 °C for 24h. Surface gloss and roughness (Ra, Rt) of each resin composite were evaluated before polishing, after polishing, and after toothbrush abrasion. Mean values and standard deviations were analysed by two way (ANOVA) (P<0.05) followed by Tukey’s post hoc test for multiple comparisons.

Results: The SEM and particle size analysis indicated that β-TCP fillers were composed of rods with an average diameter of 10 µm. The HAP fillers labelled as types A and B were spherical with an average diameter of 3-4 µm. Type C HAP consisted of rough, irregular micro-sized particles with an average diameter of 10-100 µm.

The VHN values of all the resin composites increased significantly after dry storage at 37 °C for 24h after curing. B-TCP containing resin composites exhibited highest VHN values which were directly correlated with their filler content. Whereas, the VHN values of the HAP containing resin composites increased as the filler content increased and then remained constant or decreased with further increase in filler content.

Surface gloss decreased significantly for all of the resin composites after polishing and after toothbrush abrasion. The gloss values of all the resin composites decreased as the filler content increased. β-TCP presented with highest gloss whereas Type C HAP presented with lowest gloss values.
Surface roughness increased significantly after polishing and after toothbrush abrasion for all the four types of resin composites. However, different trends in the roughness parameters were observed as the filler content was increased. Surface roughness of β-TCP containing resin composites decreased after polishing and after toothbrush abrasion as the filler content increased. Among the resin composites containing HAP fillers, types A and B surface roughness did not change significantly as the filler content increased, whereas Type C presented with highest surface roughness which was directly correlated with their filler content.

**Conclusion:** By modifying the filler content of resin composites and varying the crystal size and shape characteristics of the inorganic filler, the properties of resin composite could be modified.
Declaration

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1 Introduction and Literature Review
1.1 Structure of Teeth

Teeth constitute the hardest and most stable tissue in the human body. The structure of a tooth consists of enamel, dentine, pulp, cementum and periodontal ligament (Figure 1.1). Enamel is the hardest dental tissue and is composed of 97% mineral, 1% organic material and 2% water. The mineral exists as hydroxyapatite (Ca$_{10}$(PO$_4$)$_6$(OH)$_2$). The hydroxyapatite crystals in enamel forms well-defined rod or prism like structures with a diameter of about 4 to 8 µm. Dentine is a naturally occurring composite consisting of a microscopic filler phase of apatite crystallites and an organic matrix primarily of collagen. The apatite crystals are much smaller than the apatite found in enamel [1]. The apatite crystals in enamel and dentine contribute to strength and hardness of these dental tissues while the collagen matrix provides elasticity and resilience to the tooth structure [2].

Pulp is a soft tissue containing thin collagenous fibers, nerve cells, blood vessels etc. The cementum surrounds the root of a tooth and is composed of organic and inorganic constituents. The organic components are collagen and proteoglycans whereas the hydroxyapatite crystals constitute the inorganic component. The periodontal ligament is made of collagenous fibers and glycoproteins (protein-polysaccharide complex) and provides an attachment between the tooth and the jaw bone [1].

Figure 1.1 Structure of a Tooth [1]
1.2 Dental Caries and Restoration

Dental Caries is defined as:

“A multi-factorial disease involving interaction among the diet, saliva, the plaque micro-flora and a susceptible tooth surface”[3].

A constant process of teeth demineralisation and remineralisation occur in the enamel. Demineralisation occurs when the apatite crystals in the enamel are dissolved by acids produced by bacteria in the presence of dietary carbohydrates. Remineralisation allows the loss of calcium, phosphate and fluoride ions to be replaced by fluorapatite crystals. These crystals are more resistant to subsequent attacks by bacterial acids [4].

Dental caries occurs when there is an imbalance between demineralisation and remineralisation cycles. Caries results in cavitation and damage to the tooth structure. Damaged dental hard tissues can become a source of pain and infection. The diseased tissue has to be removed and replaced to restore form and function. For this purpose, various dental materials have been developed to act as restorative materials.

1.3 Development of Restorative Materials

Silicates were the first direct semi-aesthetic restorative materials to be introduced in the late 1800’s. They give a tooth like appearance and release fluoride throughout the life of restoration [3]. Silicates were widely used as direct restorative materials for anterior restorations until the19th century. However, due to their high solubility in oral fluids, silicate restorations had a relatively shorter life span [6].

The introduction of amalgam as a restorative material revolutionized the concept of restorative dentistry. Amalgam is produced as an alloy of silver, tin and copper with mercury. Amalgam restorations offer higher mechanical strength, higher corrosion resistance, less marginal breakdown, and lower creep as compared to the silicates [7]. For decades, amalgam has been used as a principal restorative material for posterior restorations. However, since 1990’s, there has been a rising concern regarding release of mercury vapors posing a hazard to both the dental staff and the patients [8].

More recently, a significant drift from amalgam to composite for posterior restorations has started. This is attributed to the aesthetic concerns of the patients and the concept
of minimal invasive dentistry.

1.4 Resin Composites

1.4.1 Development of Resin Composites

In 1947, direct filling acrylic methyl methacrylate resins were introduced. Acrylic resins were less soluble than silicate cements. However, they demonstrated high polymerisation shrinkage, high wear rate and interfacial discoloration [10].

Development of modern dental composites started when in the early 1960’s, Bowen investigated the possibility of reinforcing an organic polymer Bis-GMA (bisphenol A-glycidyl methacrylate) with vinyl silane (tris (2-methoxyethoxy) treated silica powder. The silane coating served as coupling agent to covalently bond the filler particles to the resin matrix. The resulting resin composites exhibited improved mechanical properties, wear resistance and colour stability [11]. However, higher polymerization shrinkage and lack of bonding to tooth structure limited the clinical success of these formulations [12].

A notable evolution was the introduction of mechanical bonding with the tooth surface. In 1950’s, phosphoric acid was used to achieve mechanical bonding with the enamel.

The development of bonding resins introduced the concept of minimally invasive dentistry. The trend of minimal invasive dentistry focused on preservation and restoration of tooth structure with as little tissue loss as possible.

More recent attention has focused on the development of resin composites with improved physical and mechanical properties, enhanced optical properties and better esthetics. These studies include changes in the composition of resin matrix, as well as concentration, morphology and distribution of the filler particles. The evolution of modern resin composites is schematically presented in Figure1.2.

1.4.2 Composition of Resin Based Composites

Resin composites are a complex mixture having resin matrix and inorganic fillers as the primary components whereas the secondary components include coupling agents, initiators and pigments.

1.4.2.1 Resin Matrix

The resin matrix consists of a synthetic monomer which is converted into a polymer by a free radical addition polymerisation reaction. The most commonly used monomers are bisphenol A glycidyl methacrylate (Bis-GMA), triethylene glycol dimethacrylate (TEGDMA) and urethane dimethacrylate (UDMA). Bis-GMA is the by-product of Bisphenol A and glycidyl methacrylate. Polymerisation of the monomer
occurs through the C-C double bond of the two methacrylate types. The chemical structure of Bis- GMA is presented in Figure 1.3.

![Chemical structure of Bis-GMA](image)

Figure 1.3 The chemical structure of Bis-GMA [14].

The structure of the molecule is stiff owing to the presence of two phenol rings in the centre and the two –OH types on the chain which form the hydrogen bonds between molecules. The molecular stiffness makes this monomer highly viscous and difficult to manipulate.

To overcome this problem, diluents monomers can be added. The viscosity of the resin formulations decreases as the percentage of the diluent monomer increases [15]. The diluent monomers include methyl methacrylate (MMA) and triethylene glycol dimethacrylate (TEGDMA). The molecular structure of TEGDMA is flexible due to weak polar bonds in the chain. This addition helps to reduce the viscosity and facilitates filler loading. However, TEGDMA can contribute to an increase in polymerization shrinkage [16]. The chemical structure of TEGDMA is presented in Figure 1.4.

![Chemical structure of TEGDMA](image)

Figure 1.4 The chemical structure of TEGDMA [14].

UDMA resins have low viscosity and enable maximum filler loading and possess higher degree of conversion as compared to Bis-GMA [17]. UDMA is composed of flexible ether bonds which increases the flexibility of the monomer. They possess lower water sorption and increased fracture toughness [18]. Based on these properties, UDMA resins were selected in the present study to prepare the experimental resin
composites. Their disadvantages, however, are brittleness and their polymerisation shrinkage of about 5-9% [19].

![Figure 1.5 The chemical structure of UDMA][14]

### 1.4.2.2 Fillers

Filler is the solid additives incorporated into the polymers to modify the physical and mechanical properties. In resin composites, filler particles constitute the inorganic phase. Commonly used fillers are quartz, fused silica and glasses like alumino-silicates, borosilicates and silicion dioxide.

In recent years, there have been increasing amount of studies investigating the effect of filler morphology and content on the properties of the resin composites. Fillers act as strengthening agents and reduce the dimensional changes in the resin composites. They reduce the thermal expansion coefficient [20], the overall curing shrinkage [21] and improve the handling of the resin composites [22]. It has been demonstrated that elastic properties [23] and mechanical properties such as compressive and flexural strength of the resin composites improve as the amount of filler increases [23,24].

The influence of filler morphology on the properties of resin composites has been studied extensively. Previous studies suggest that as the filler particle size becomes smaller, the restoration has a better finish and polishability [25]. This improves the surface texture and reduces the likelihood of biodegradability. The small filler particles also lead to reduced polymerisation shrinkage [26] and reduce the probability of microfissures and cracks which are responsible for post-operative sensitivity and restoration failure [22].

### 1.4.2.3 Coupling agents

Coupling agents are added to filler particles to improve the adhesion between inorganic filler and the organic matrix. It has been demonstrated that coupling agents provides a critical link between matrix and filler (Figure 1.6). This bond helps in stress
distribution over the bulk of the restoration by directing the load from the weaker organic matrix to the fillers that possesses better mechanical properties [27]. They also improve the dispersion of filler in the organic matrix [27].

Silane coupling agents act as soap to reduce the surface tension between inorganic filler and organic matrix and reduce the viscosity of the resin composites [28]. They improve the mechanical properties of composites such as improve the wear rate [29], increase the interfacial shear strength of the filler particle to the resin matrix [30] and improve the flexural strength of the resin composite [31].

Commonly used coupling agents are epoxy, vinyl and methyl silanes. The most widely used coupling agent is 3- methacryloxypropyltrimethoxysilane (MPTS).

![Silane bonding diagram](image)

Figure 1.6 Schematic representation of Silane bonding between the fillers and resin matrix [28].

Silane coupling agents have silanol (Si-OH) on one end and methacrylate group (containing C=C) on the other end. These molecules form covalent bonds with the fillers on one end and with the methacrylate types of the resins at the other end as presented in Figure 1.6. In the present study, the HAP fillers were not modified with coupling agents as the purpose was to study the properties of unmodified HAP fillers.

1.4.2.4 Activation and Initiation Systems

Initiators are used to begin the process of polymerization by formation of free radicals. These free radicals can be generated by heat, chemicals, ultraviolet and visible light.
Virtually all modern direct composites are polymerized by photo activation where light is applied to single paste formulations. The first light-activated systems utilized ultraviolet light to generate free radicals. These materials contain initiators such as benzoin methyl ether. However, the ultraviolet radiations are scattered by filler particles resulting in curing depth less than 1 mm. To overcome these problems, visible light activated systems were developed. These systems are composed of diaketones such as camphorquinone as photoinitiators. The visible light activated systems have improved working time, depth of cure and better colour stability [32].

Over the past few years, a wide range of visible light curing units have been developed. They include light curing sources such as quartz tungsten halogen, argon laser plasma arc and light emitting diode (LED). These light sources differ in the mode of light emission, light intensity, spectral emission, and the exposure time required to cure the materials. Previous studies have reported that higher intensity of curing light can improve the physical and mechanical properties of the resin composites [33]. LED units have certain advantages over the halogen curing units. These include low power consumption, lower heat generation and high curing efficacy. They produce a narrow spectrum of blue light in the 400-500 nm range which is the most effective energy range to activate camphorquinone photo initiators in the resin based composites [34, 35]. In the present study, camphorquinone was used as an initiator to prepare the experimental resin composites.

1.4.2.5 Inhibitors

Inhibitors are added to prevent polymerization of the monomer under storage conditions. The most commonly used inhibitors are butylated hydroxytoulenes (BHT) and monomethyl ether of hydroquinone. In the present study BHT was used as an inhibitor for the experimental resin composites.

1.4.2.6 Pigments

The resin composites are blended with dyes and pigments to approximate the natural shade of teeth. Examples include cadmium orange, cadmium yellow, fluorescent zinc oxide, titanium dioxide, etc. [1]. In the present study, pigments were not used as the purpose was to study the properties of fillers a without any addition of pigments and additives in the organic matrix of the experimental resin composites.
1.4.3 Classification of Resin Based Composite

Many studies have attempted to classify resin composites but it is complex owing to the variations in their filler size, clinical applications and consistencies. Lutz et al. presented a classification which divided composites into conventional, micro-filled, and hybrid composites, based on the filler particle size [36].

1.4.3.1 Macro-filled Resin Composites

Macro-filled resin composites are named as traditional or conventional composites. Traditional composites were prepared by adding irregular shaped quartz and glass filler particles ranging from 1 to 100 µm to resin matrix (Figure 1.7). They have a reduced surface area to volume ratio and hence reduced bonding between resin and filler particles. This causes the dislodgement of resin particles and results in the large wear facets and craters in the restoration [37].

Moreover, the restorations appear dull and have rough surface. The rough surface serves as a niche for plaque accumulation [36]. In order to overcome these problems, resin composites with smaller and uniform filler particle size were developed.

Figure 1.7 Schematic representation of traditional resin based composites (RBCs) illustrating filler particles of approximately 1-30 µm size [6].

1.4.3.2 Micro-filled Resin Composites

In 1970s and in 1980s, microfilled composites with an average filler particle size with 1µm were developed (Figure 1.8). These materials had improved polished surface as compared to the traditional resin based composites owing to their particle size smaller
than the wavelength of visible light. Theoretically, micro filled composites were actually nano composites with the nano sized particles. But since the concept of nanotechnology was not yet known, they were categorized as micro- filled resin composites.

The reduced filler particle size led to an increase in the surface area to volume ratio which limits the amount of filler particles that could be incorporated in composites. Moreover, these composites had high viscosity and difficult handling properties as compared to the traditional composites [36]. In order to overcome these problems, monomers containing pyrogenic silica particles less than 100 nm in diameter were incorporated into pre-polymerized organic fillers. This resulted in the formation of heterogeneous microfilled composite. These heterogeneous microfilled composites possess better polishability and aesthetics [11]. However, their wear resistance, elastic modulus and fracture strength are inferior to macrofilled composites [38]

![Figure 1.8 Schematic representation of (a) homogenous microfilled and (b) heterogeneous microfilled RBCs. Heterogeneous microfilled RBC shows prepolymerised filler particles of approximately 25 μm size in contrast to homogenous microfilled RBC [6]](image)

1.4.3.3 Hybrid Resin Composites

Hybrid resin composites were developed to retain the properties of both the macrofilled and microfilled resin based composites. The distribution of particle size allowed increased filler loading ranging from 70-80 wt% of the filler content. Conventional hybrid composites are composed of bimodal distribution of particle size
with large particles ranging from 1 to 5 µm and the smaller particle of 0.05 µm in diameter [38].

Hybrid composites possess increased hardness and mechanical strength, lower coefficient of thermal expansion [39] and lower polymerization shrinkage [11, 39]. These composites have a better wear resistance than conventional and microfilled resins [37, 40, 41]. However, because of the presence of larger filler particles they still had compromised surface properties [11].

To overcome these problems, microhybrid resin composites with filler particle size ranging from 0.01 to 6 µm (Figure 1.9) were developed. These particles were produced by sol-gel procedure that resulted in uniform round shaped particles. Microhybrid resin composites offer improved polished surface, better handling properties and abrasion resistance as compared to composites with bimodal distribution of filler particles [37, 40, and 41].

Figure 1.9 Schematic representation of (a) conventional hybrid (b) microhybrid RBCs showing smaller filler particle size compared with conventional hybrid RBC [6].

During the past ten years, materials scientists have demonstrated that the average particle size of the inorganic fillers should range below 1 to 3 µm to provide good polishability and high abrasion resistance [14].

1.4.3.4 Nano composites

Nanotechnology can be defined as, “the construction of materials and structure size of 1 to 100 nanometers or less with novel characteristic through manipulating, measuring and modelling of matter on a molecular scale” [42]
In 2003, novel resin based nano composite were introduced. These nano composites combined the aesthetic properties of microfill and excellent mechanical properties of hybrid composites [43]. The physical and mechanical properties of nano composites were superior to hybrid and microfilled composites [44].

Significant improvement in surface smoothness and polish retention have been reported for nanofills compared with conventional microfills. Moreover, nano composites allow increased filler loading leading to increased strength and reduced polymerization shrinkage [44, 45].

Nano composites are available as nano hybrids and nano fills. Nano hybrid is composed of milled glass filler and discrete nanoparticles (40-50 nm). Whereas, nano fill is composed of both nano sized particles, called nanomers and agglomerates of nano sized fillers named as “nano clusters”. These nano clusters reinforce the resins and improve the strength of the restoration [45]. A summary of the different fillers used in the different types of resin composites is presented in Table 1.1.

Table 1.1 Fillers in resin based composite materials [38]

<table>
<thead>
<tr>
<th>Composite type</th>
<th>Filler size (µm)</th>
<th>Filler</th>
</tr>
</thead>
<tbody>
<tr>
<td>Macro filled</td>
<td>5 – 30</td>
<td>Quartz or Glass</td>
</tr>
<tr>
<td>Micro filled</td>
<td>0.01 – 0.1</td>
<td>Colloidal Silica</td>
</tr>
<tr>
<td>Hybrid</td>
<td>1 – 20 and 0.01 – 0.05</td>
<td>Glass and Colloidal Silica</td>
</tr>
<tr>
<td>Modern hybrid</td>
<td>0.5 – 1 and 0.01 – 0.05</td>
<td>Glass, Zirconia, colloidal silica</td>
</tr>
<tr>
<td>Nano Filled</td>
<td>&lt; 0.01 (10 nm)</td>
<td>Silica or Zirconia</td>
</tr>
</tbody>
</table>

1.4.4 Properties of Resin Based Composites

1.4.4.1 Degree of Conversion of Resin Based Composites

Degree of conversion (DC) is the percentage of reacted C=C bond in the course of the addition polymerisation of monomer. The degree of conversion ranges from 55 to 75% under conventional light activation [46].
Degree of conversion depends upon several factors such as type and structure of the monomer, filler composition and particle size, the photoinitiator, the exposure time, and the intensity of the curing light [47]. The degree of conversion influences the hardness [48], mechanical properties [47] and biocompatibility of resin composites [51].

When curing composite resin, it is essential to have an adequate light penetration throughout the bulk of the resin composite. However, some degree of scattering occurs which results in the reduction of penetration of light to the photo initiator in the deeper parts of the restoration. Therefore, the degree of conversion varies throughout the bulk of restoration as it is dependent on the absorption of photons from light energy activation. Light scattering is directly related to the type, amount and size of the filler particle [49]. Light scattering reaches its maximum when the particle size reaches a value of approximately half of the wavelength of light [49]. Hence the degree of conversion decreases in the resin composites with smaller filler particles [50]. To avoid excessive light scattering, a resin composite should have the filler and resin matrix with similar refractive indices, uniform particle size distribution and regular shape of filler particles [50, 51].

Direct methods used to measure the degree of conversion include infrared spectroscopy and laser Raman spectroscopy. These methods are complex, expensive and time consuming. Degree of conversion can be measured by indirect methods such as visual, scraping and surface hardness measurement. Surface hardness is a good indicator of degree of conversion. The greater the monomer conversion, the higher is the surface hardness of a resin composite [47].

\subsection{Surface Hardness of Resin Composites}

Hardness is defined as the resistance of a material to indentation [1]. It predicts the wear resistance of a material and its ability to withstand abrasion and attrition. In order to resist masticatory forces and achieve optimum clinical performance in the stress bearing areas of the mouth, the restoration should have adequate surface hardness.

The hardness of resin composites depends on parameters such as morphology, particle size [25], type and amount of filler particle [52]. Reduction in the filler particle size, increase in the interfacial area between resin and filler results in an increase in the
hardness of the resin composite. Hardness is linearly proportional to the content of filler loading in the resin composite [25, 53]. Filler loading also depends on the morphology of the filler particles. Resin composites with round shaped filler particles have high filler loading and possess increased hardness as compared to resins with irregularly shaped filler particles [52].

The hardness of a material can be measured by indentation test which measures the ability of the material to be indented by another material. Hardness indentation tests are usually classified in two categories; macroindentation tests (load > 1 kg) and micro indentation tests (load < 1 kg). Micro hardness refers to the hardness testing of materials with low applied loads. Micro indentation tests are used in dentistry because of the smaller dimension of the materials. The most commonly used micro hardness tests are Knoop hardness and Vickers tests.

The Knoop hardness tests employs the use of a static diamond tip under a specific load to form a microscopic indent over the tested material over a specific period of time. This method is used for polymeric materials such as resin composites as it minimises the effect of elastic recovery [54]. Vickers hardness test employs a square shaped intender and is used for brittle materials. The hardness number is calculated by dividing the load by the surface area of indentation. The Vickers hardness test is most commonly used for measuring the surface hardness of dental resin composites.

1.4.4.3 Surface Roughness of Resin Composites

Surface roughness can be defined as the irregularities in the surface texture, which occur due to the inherent nature of the material [55]. A smooth surface finish is clinically important for the longevity of the restorations. Irregularities in the surface of a restoration can lead to plaque accumulation [56] and subsequent secondary caries leading to failure of the restoration [57]. Additionally, rough occlusal composite restoration surfaces can cause excessive wear of the opposing enamel [58].

Surface roughness can be measured by various methods including contact stylus tracing, scanning electronic microscope, laser reflectivity and non-contact conofocal microscopy. A 3-D non-contact stylus profilometer is most commonly used which has the advantage of rapid quantitative measurement without damaging the specimen.

Vertical roughness parameters, Ra and Rt are used to describe the surface roughness.
Ra is most commonly used to estimate the surface quality of resin composite materials in amplitude.

Surface roughness parameters are dependent on factors such as filler structure, percentage of surface area occupied by filler particle, filler–resin matrix interaction and the coupling agents [59, 60]. Smooth surface of a resin composite restorations could be obtained by curing against the polyester strip [48]. This occurs due to the formation of a smooth resin-rich layer over the surface by adaptation to the polyester strip. However, this layer is weak and it has to be contoured and polished to improve aesthetics, wear resistance and marginal integrity [44].

1.4.4.4 Wear Resistance of Resin Composites

Wear could be defined as the gradual removal of the material surfaces which occurs as a consequence of interaction between surfaces moving in contact with each other [61]. Composite restorations are prone to wear under masticatory forces, toothbrushing and abrasive food. Wear resistance is important in determining the longevity of a restoration. Wear occurs as a result of several material specific parameters such as contact force, sliding friction, physical and chemical interaction in the oral environment. There can be two types of wear in the oral environment.

1.4.4.4.1 Two Body Wear

Two body wear occurs when there is direct contact between the restoration and the opposing or adjacent teeth.

1.4.4.4.2 Three Body Wear

Three body wear occurs as a result of food bolus between occlusal surface or from toothbrush with toothpaste dentifrice. Several studies have used simulated toothbrush abrasion test to predict the three body abrasive wear behaviour of restorative materials.

The wear resistance of the resin composites can be improved by improving the chemical stability of the resin and silane coupling agent [11]. The filler particle size also affects the abrasion resistance of the resin composite [62]. Small sized particles result in reduction of inter particle spacing in the resin matrix by allowing higher filler loading and stronger interaction with the resin particles [63, 64].
1.4.4.5 Surface Gloss of Resin Composites

Surface gloss plays an important role in the aesthetic appearance of restorations and their blending to surrounding teeth. It is the measure of specular reflection which is the light reflected uniformly into a single outgoing direction. The specular reflection of the polymer depends upon the refractive indices of the media [65]. In resin composites, surface gloss depends upon the refractive indices of the resin matrix and the filler particles [66]. The surface gloss reduces when there is a mismatch between the refractive indices of the resin and the filler [67].

Furthermore, the surface gloss of the resin composite decreases if the light is scattered by the filler particles. It has been observed that light scattering by fillers is linearly related to filler content [68]. In addition, surface gloss of the resin composites also strongly depends on the filler particle size [25]. Resin composites with smaller filler particles have a glossier surface when polished as compared to fillers with larger particle size. Previous studies suggest that polishable resin composites with filler size ca. 0.5 µm possess initial high gloss and retain it over an extended period of time [69].

Numerous studies suggest that surface gloss is negatively related to roughness. For example, microfilled resin-composites were shown to have a low roughness and consequently a higher gloss [70]. This implies that decreasing roughness of a material, gloss should increase [66].

1.4.4.6 Polishability of Resin Composites

Mylar strips (polyester matrix film) provide the smoothest resin composite surface. However, their use is limited because of the complex tooth anatomy. In addition, the surface of the restoration is rich in resin content which reduces the wear resistance of the restoration [69]. Therefore, finishing and polishing of composite materials after placement are required to improve aesthetics and early wear resistance. Currently wide variety of finishing and polishing instruments are used such as tungsten carbide finishing burs, hard bonded-surface coated ceramic diamond rotary instruments, impregnated rubber or silicone discs and wheels and silicon carbides or aluminium oxide-coated abrasive discs [58]. The final polished surface depends upon the polishing system and filler features such as size, shape, and filler content of the resin composite. The larger the filler particles, the rougher the surface is after polishing
In addition, smaller filler particles have a glossier finish when polished as opposed to resin-composites with larger fillers [69]. Nanofill resin composites with high filler loadings best withstand the finishing and polishing procedures [58].

1.5 Bioactive Restorative Materials

An ideal restorative material is biocompatible, long-lasting and aesthetically acceptable. Dental restorations have been considered as a non-biologic substitute. Recent developments have resulted in development of restorative materials with improved physical and mechanical properties and excellent aesthetics. These materials replace the tooth structure and play their role in aesthetics and function but these restorations have a limited lifespan because of recurrence of caries under the restoration. Secondary caries is the most important factor for replacement of resin based composite restorations [5]. Recent studies have attempted to develop bio-active restorative materials that could reverse the caries process as well as remineralise the decayed tissue.

Over the last 25 years, fluorides have been used widely to promote the remineralisation of the enamel lesions. However, there are some rising concerns over the excessive use of fluorides in both prescription and over the counter dental formulations. Recent evidence suggests that chronic low-level exposure to fluoride can present problems in organ system gastro-intestinal, genito-urinary and respiratory system [71]. Therefore, material scientists are investigating other alternatives which can induce remineralisation by re depositing the minerals lost in caries process without harmful systemic effects.

Calcium and phosphate are the principal minerals in bone, enamel and dentine and make up more than 95% and 60% by weight of the enamel and dentin respectively [71] For this purpose, calcium phosphate compounds have gained a lot of attention in recent years due to the similarities in their chemical composition with teeth and bone. These compounds such as tricalcium phosphate and hydroxyapatite are being investigated extensively to promote tooth remineralization and regeneration.
1.6 Tricalcium Phosphate

In recent years, several bioactive compounds such as such as amorphous dicalcium phosphate (DCPA) and Tricalciun phosphate (TCP) have been developed that release calcium and phosphate ions in the presence of an aqueous solution, which then precipitates to form hydroxyapatite [73]. They are used primarily in combination with other compounds or with fluorides and are available in toothpastes, fluoride varnishes, chewing gums and mouth rinses [74].

Tricalcium phosphate (Ca$_3$(PO$_4$)$_2$) (TCP) exists in many polymorphs phases such as α, β and γ. However, only α and β-TCP are used as biomaterials [72]. β-TCP has been used as capping agent, for cleft palate repair and apical barrier formation in root canal therapy [73]. Previous studies have suggested that β-TCP induced formation of mineralised tissue within the root canal [72].

β-TCP has been shown to effectively remineralise enamel and dentin lesions in vitro [75]. Previous studies indicate that β-TCP has a tendency to produce large amount of reparative dentine [76]. Previously, DCPA nanoparticles have been incorporated into experimental dental resin composites which showed promising results for both caries-inhibiting and stress-bearing capabilities [77]. However, there has been no investigation on using β-TCP particles as fillers in dental resins composites.

Accordingly, the objectives of the present study are to use β-TCP filler particles to formulate a series of resin composites and study their effects on the key properties of resin composite.

1.7 Hydroxyapatite

Hydroxyapatite (Ca$_5$(PO$_4$)$_3$(OH) (HAP) is a naturally occurring mineral. Hydroxyapatite is the most documented biomaterial owing to its excellent biocompatibility and ability to stimulate osseointegration. It is the most widely used bioactive material in orthopedics and dentistry. Their clinical applications include repair and regeneration of bone defects, drug delivery devices, coatings for implants and as scaffolds for dentine regeneration [78]. It is chemically similar to bones, dental enamel and dentine. The chemical comparison of hydroxyapatite with teeth and bone is presented in Table 1.2
Table 1.2 Chemical Comparison of teeth, bone, and hydroxyapatite [79]

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Enamel</th>
<th>Dentine</th>
<th>Bone</th>
<th>Hydroxyapatite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium (wt%)</td>
<td>36</td>
<td>35</td>
<td>34</td>
<td>39</td>
</tr>
<tr>
<td>Phosphorus (wt%)</td>
<td>17</td>
<td>16</td>
<td>15</td>
<td>19</td>
</tr>
<tr>
<td>Ca/P</td>
<td>1.73</td>
<td>1.67</td>
<td>1.71</td>
<td>1.67</td>
</tr>
<tr>
<td>Total Inorganic %</td>
<td>97</td>
<td>70</td>
<td>65</td>
<td>100</td>
</tr>
<tr>
<td>Total Organic %</td>
<td>1.5</td>
<td>20</td>
<td>35</td>
<td>----</td>
</tr>
<tr>
<td>Water%</td>
<td>1.5</td>
<td>10</td>
<td>10</td>
<td>----</td>
</tr>
</tbody>
</table>

1.7.1 Remineralisation Potential of Hydroxyapatite Based Dental Materials

The remineralisation potential of nano hydroxyapatite (nano-HAP) has recently been highlighted. Nano-sized hydroxyapatite particles have similar morphology and crystal structure to the apatite crystal found in tooth enamel [85]. Nano-HAP possesses better bioactivity than the micro sized HA and initiates improved osseointegration in orthopaedic and dental formulations [83]. A previous study has demonstrated that nano- HAP crystals adhere and aggregate and grow into uniform apatite layer on the demineralised surface. The specimens treated with synthetic nano-HAP exhibited surface Ca/P ratio close to that of the biological enamel indicating apatite deposition on the demineralized enamel surface. Whereas, when the demineralised enamel was treated with fluoride, only structural modification occurred and the Ca/P ratio did not change. [84]

The remineralisation potential of nHAP has been studied by incorporating nHAP particles in various dental products. Mouthwashes containing nano hydroxyapatite in combination with sodium fluoride indicated that remineralisation was increased in primary carious lesions [85]. Tooth pastes containing nano hydroxyapatite demonstrated that nano hydroxyapatite had a significant effect on remineralisation when compared to tooth paste containing fluoride amine as mineralizing agents [86]. Fissure sealants containing NHAP can induce remineralisation in the region immediately beneath the sealant. [87]
In addition, visible light curing resin based cavity liner that contain hydroxyapatite fillers have been commercialized. They are known to be beneficial to tooth structure by promoting secondary dentine formation and possess cariostatic properties.

1.7.2 Hydroxyapatite Based Resin Composites

The addition of HAP as fillers to resin composites was first reported in 1988 which resulted in an improvement of mechanical properties and biocompatibility [88]. It was suggested that the properties of HAP resin composite depend upon factors such as filler content [89, 90], particle size, shape [89] and their distribution [67].

The mechanical properties of the HAP based resin composites depend upon the concentration of HAP in the composite. A previous study on mechanical properties proposed that addition of HAP should be 50-60 wt/wt% to improve the mechanical properties [89]. In contrast, a few studies suggested that HAP can improve the mechanical properties of composites at low loading ratios. If, however, it exceeds certain limit, it may negatively influence the mechanical properties [90]. Another study suggested that the critical mass fraction should be around 10% to influence the mechanical strength [90].

HAP fillers can be used as micro and nano sized crystals. Previous studies suggested that nHAP improve the compressive, diametric tensile and biaxial flexural strength [87, 91]. It was demonstrated that nHAP increases the bond strength between the resin and tooth structure makes them effective in very low concentration. Nano- HAP significantly improved the compressive strength of resin composite at a concentration of 5 and 10 % [92]. In addition, Nano-HAP possess increased tendency to initiate remineralisation [93]. In contrast, a few studies preferred micro HAP over nano-Hap on the basis of hydrolytic stability, surface roughness [89], mechanical strength and surface hardness [67]. It was suggested that nano- HAP have increased water solubility [94] and tendency to form agglomerates which compromises their mechanical strength [89].

The main concern over the HAP composites were compromised mechanical properties. However, previous studies have suggested reinforcement techniques to improve the mechanical strength of HAP based experimental resin composites.
Various methods of reinforcement have been developed including incorporation of nano-rods [95], whiskers [95] and preparation of particles with high –aspect ratio in order to improve the mechanical strength of the HAP based resin composite [97].

Understanding the structure-properties relationship is important for the development of new materials and the improvement of the existing ones. To date, a significant number of studies have been done on the properties of resin composites containing different types of fillers with variable loading rates and particle sizes. However, there are limited studies to compare and correlate the effects of β-TCP and HAP filler particles on the properties of resin based composites. In the present study, β-TCP and HAP powders with different crystal structure, particle size and loading ratios were used to prepare resin based composites to study the influence of structure and loading ratio on the key properties of the experimental resin composites.
Aims & Objectives

Aims

To enhance understanding of the relationship between structure and properties of tricalcium phosphate and hydroxyapatite containing experimental resin based composites.

Objectives

1. To study the particle size and morphology of β-TCP and three types of HAP powders.

2. To formulate a series of β-TCP or HAP containing experimental resin composites.

3. To measure properties such as surface hardness, surface roughness and surface gloss of the experimental resin composites.

4. To correlate structures and properties of the experimental resin composites

5. To study the influence of filler content on the properties of experimental resin composites.
2 Materials and Methods
2.1 Fillers

β-TCP and three types of hydroxyapatite powders (Budenheim, Germany, Table 2.1) were used in the present study to prepare resin composites containing hydroxyapatite fillers.

Table 2.1 Fillers used to prepare the experimental resin composites

<table>
<thead>
<tr>
<th>Filler</th>
<th>Chemical Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>C73-13</td>
<td>Beta Tricalcium bisorthophosphate</td>
</tr>
<tr>
<td>C73-08</td>
<td>Pentacalcium hydroxide triorthophosphate</td>
</tr>
<tr>
<td>C13-09</td>
<td>Pentacalcium hydroxide triorthophosphate</td>
</tr>
<tr>
<td>Ossea Cafosa</td>
<td>Ossea Cafos Mg</td>
</tr>
</tbody>
</table>

The particle size of the fillers used in this study was measured using a laser diffraction particle size analyzer (Beckman Coulter LS 13 320, CA, USA). The particle size distribution of the fillers was presented in volume % in a range of 0.04 to 2000 μm.

The filler morphology was investigated by a scanning electron microscopy (SEM, FEI Inspect F, Oxford Instruments, UK). Filler powders were attached to standard SEM alumina specimen stubs by carbon conductive adhesive tapes (Agar Scientific, UK). Specimens were gold coated for conductivity and to avoid charge accumulation. Specimens were then loaded into the specimen chamber of the scanning electron microscope. A working distance of 10 mm was used. Images of the filler powders with various magnifications were taken at an accelerating voltage of 10 KV. The elemental composition of the fillers was investigated using the energy dispersive X-ray spectroscopy equipped with the SEM on carbon coated samples.

2.2 Filler Density Estimation

Fillers were packed in a container of known volume (7 ml) using a calibrated electronic analytical balance with an accuracy of 0.1 mg (Ohaus Analytical Plus,
The apparent powder density was calculated as the interparticle voids and pores were not taken into consideration. The powder density of fillers was estimated by the following equation

\[ \text{Density} = \frac{\text{Mass}}{\text{Volume}} \]

### 2.3 Compositional Design of the Experimental Resin Composites

The organic matrix comprised of Urethane dimethacrylate (UDMA), Camphorquinone (CQ) and Dimethylamino ethyl-methacrylate (DMAEM). CQ and DMAEM comprised the photo-initiator system in a ratio of 0.5 and 1 wt. % respectively. Butylated Hydroxytoulene (BHT) (0.01 wt. %) was added as an inhibitor to prevent polymerisation under storage conditions. The constituents of the organic matrix of the experimental resin composites are listed in Table 2.2.

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Chemical Name</th>
<th>Product Number</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>UDMA</td>
<td>Urethane dimethacrylate</td>
<td>436909</td>
<td>Sigma Aldrich, UK</td>
</tr>
<tr>
<td>CQ</td>
<td>Camphorquinone</td>
<td>272078</td>
<td>Sigma Aldrich, UK</td>
</tr>
<tr>
<td>DMAEM</td>
<td>2(dimethylamino)ethyl-methacrylate</td>
<td>234907</td>
<td>Sigma Aldrich, UK</td>
</tr>
<tr>
<td>BHT</td>
<td>Butylated Hydroxytoulene</td>
<td>1082708</td>
<td>Sigma Aldrich, UK</td>
</tr>
</tbody>
</table>

In order to study the effect of different types of fillers loading on the properties of resin composites, the fillers were systematically incorporated to the organic matrix by increasing the loading ratio. Five resin composites with a filler mass fraction ranging from 20% to 60% were prepared for each filler type.
2.4 Preparation of Experimental Resin Composites

The filler powders and the organic matrix components were weighed on a precision calibrated balance (Ohaus Analytical Plus, Ohaus Corporation, USA) with an accuracy of 0.1 mg. The components were added to an opaque container and were mechanically mixed using a speed mixer (DAC 150.1 FVZK, UK) (Figure 2.1). The container carrying the mixture was secured in a holder in the upper compartment of the speed mixer. The mixing speed and time were adjusted on the speed control dial to 3000 rpm for 2 minutes. This combination of speed and time was based on a previous study on bioactive resin composites [98].

After the completion of the mixing cycle, the container was removed from the speed mixer. The mechanical mixing resulted in a homogenous paste. The resin composites were stored in dark containers in the laboratory refrigerator at 4°C.

Figure 2.1 Speed Mixer
2.5 Filler Volume Fraction Calculation

In order to calculate the filler volume fraction, the densities of the experimental composites were estimated by the method described in section 2.2. The density of filler was estimated already as discussed in section 2.2. The filler percentage by weight in each resin composite and the densities of respective filler and resin composites were used to calculate their filler volume fraction by using the following equation:

\[
\text{Volume (\%) filler} = \frac{\text{Mass (\%) filler} \times \text{Density of resin composite}}{\text{Density of filler}}
\]

2.6 Vickers Micro-Hardness

2.6.1 Specimen Preparation

The experimental resin composites were packed into Teflon moulds (Diameter: 2 mm; Height 2 mm) and pressed on both sides with two microscopic glass slides to extrude excess material out of the mould and to achieve a flat surface. Specimens were then irradiated for 40 seconds with a visible light LED curing unit (Elipar S10, 3M ESPE, Germany) with a tip diameter of 10 mm. Five specimens were prepared (n=5) for each composite type. The top surfaces of all specimens were ground with P1000 silicon carbide paper (3M ESPE, USA) to remove the resin rich layer.

2.6.2 Vickers Micro-Hardness Measurement

Vickers micro-hardness was determined using a Micro-hardness instrument (FM-700, Japan (Figure 2.2) equipped with a Vickers diamond indenter (diameter: 10µm).

Vickers micro-hardness (VHN) was measured immediately after curing and after dry storage at 37± 1°C for 24 h. Micro-hardness was measured under a load of 300 g for 15 seconds at room temperature (23± 1°C). Three equally spaced indentations were randomly measured on each specimen. The indentations were made 1mm away from the margins of the specimen. A distance of 1 mm was allowed between the three indents. An average of the VHN values was used to work out hardness of the resin composites.
2.7 Surface Gloss

2.7.1 Specimen Preparation

To measure the surface gloss, five disk-shaped specimens (diameter: 6 mm; height: 2 mm) were prepared (n=5) for each resin composite. Uncured resin composite was loaded in the custom-made Teflon moulds (Figure 2.3) and covered on both sides with transparent polyethylene strips. Each mould was compressed between two microscopic glass slides to extrude excess material and to obtain a flat surface. The top surfaces of all samples were irradiated for 40 seconds with a LED light curing unit (Elipar S10, 3M ESPE, Germany) having a tip diameter of 10mm. The top surfaces of all the specimens were ground with P1000 silicon carbide paper (3M ESPE, St Paul, MN, USA) to remove the resin rich layer over the surface.
2.7.2 Finishing and Polishing

Specimens were finished with a sequence of 400, 600, 800 and 1200 grit Silicon carbide (3M ESPE, St Paul, MN, USA) papers under continuous water. The top surfaces of all specimens were polished using OptiDisc system (Kerr, KerrHawe, Switzerland).

Samples were sequentially polished from finish to high gloss. Each polishing disk was used for 30 seconds with a slow hand piece rotating at approximately 10,000 rpm. Finally, the specimens were washed and gently air-dried to remove any residual.

2.7.3 Surface Gloss Measurement

The surface gloss of the specimen was measured using a glossmeter (Novo Curve Rho point, Bexhill on Sea, England). The instrument is capable of measuring the intensity of a reflected light beam after striking the test surface at an angle of 60° and comparing with a reference value. The instrument has a window of 2 x 2 mm over which the specimen was placed and covered with a film container to avoid external light exposure during the measurement.
Three readings were performed at the center of each specimen by turning specimen by 90°. The average of the three measurements was recorded for each specimen. The surface gloss was measured before and after simulated toothbrush abrasion.

2.8 Simulated Toothbrush Abrasion

Specimens were subjected to wear by using a custom-built tooth brushing simulator (Figure 2.5). The instrument has four separate reservoirs with separate toothbrush holders. The toothbrushes are motor-driven and move in a back and forth direction. The instrument is equipped with an inbuilt meter to record the number of brushing strokes. The instrument is designed to deliver the tooth brushing strokes at a rate of 78 cycles per minute.

One specimen was fixed to a holder on the base of each reservoir as shown in Figure 2.5. Four specimens were tested simultaneously for simulated tooth brushing during each cycle. Each reservoir was filled with 150 g of abrasive slurry prepared by a dentifrice containing aluminium hydroxide (Colgate Total, Colgate-Palmolive, UK) with relative dentine abrasivity (RDA) of 70. The slurry was prepared with a paste to water ratio of 2:1.

Plane toothbrush head (Oral-B 40 Indicator, Regular) with rounded bristles was fixed to each toothbrush holder. All specimens were subjected to a total of 10,000 reciprocal
strokes. The instrument was set to provide a vertical load of 2.5 N on each specimen. After testing, specimens were removed from the machine, rinsed with tap water and gently air dried. The toothbrushes and slurry were replaced before each new testing cycle.

Figure 2.5 Toothbrushing Simulator

Figure 2.6 Schematic diagram of tooth brushing simulator. (A) 2.5 N metal load, (B) Toothbrush holder, (C) Toothbrush head, (D) Composite specimen, (E) Glass reservoir, (F) Silicon mould.
2.9 Surface Roughness

2.9.1 Specimen Preparation

Specimens were prepared as described in section 2.7.1.

2.9.2 Surface Roughness Measurement

Surface roughness of each specimen was determined using a non-contact optical profilometer (CLI 1000, Taylor Hobson Limited, UK) (Figure 2.7). Specimen was placed over a flat surface and scanned by a confocal optical sensor with 0.25 mm cut-off length. The gauge selected for scanning was CLA 3 mm having a sampling rate of 500 Hz. The direction of measurement was adjusted to east to west plane i.e. from right to left. For each specimen the maximum spacing between scanning points was adjusted to 10 µm. The speed was adjusted to 5 mm/s across the surface. Scans were performed on a region of 1 x 1 mm2. Three readings were performed on each specimen surface.

Figure 2.7 Talysurf CLI 1000 Profilometer
The data obtained was analysed with TalyMap software (Taylor Hobson, UK) to obtain 2D and 3D surface profiles and calculate surface roughness parameters. Following parameters were measured for 2D surface analysis as described in Figure 2.8.

**Ra**: It is the most commonly used parameter in surface roughness analysis. It is the arithmetic mean of the absolute departures of the roughness profile from the mean line.

**Rt**: It is the vertical height between the highest and lowest point of the profile within the assessed area

![Diagram of surface roughness parameters](image)

Figure 2.8 Surface roughness parameters (A) Ra (B) Rt

where Rq: root mean squared; M: mean line; Rv: maximum valley depth; Rp: maximum peak height

### 2.9.3 Surface Roughness Measurement after Toothbrush Abrasion

After simulated tooth brushing, specimens were placed in an ultrasonic water bath
(Elma ultrasonic T310, Singen, Germany) for five minutes to remove any surface debris. The specimens were scanned for surface roughness analysis immediately after cleaning and air drying.

2.10 Statistical Analysis

The vickers micro hardness, surface gloss and surface roughness values of the resin composites were compared by two-way ANOVA, one-way ANOVA and Tukey’s multiple comparison tests (p <0.05) using a statistical software (SPSS Version 22, New York USA). Linear regression analysis was performed to analyse the correlation between the properties of the resin composites and the filler loading.
3 Results
3.1 Structure of the Fillers

In the present study, the morphology of the filler particles was studied under a scanning electron microscope (FEI Inspect F, Oxford Instruments, UK). The SEM analysis showed that the β-TCP and the three types of hydroxyapatite fillers presented with significantly different morphologies.

B-TCP filler consisted of rod-shaped particles having a diameter of several hundred nanometers with a high aspect ratio (Figure 3.1). Type A (HAP) particles were fine particles with a size between 1to 4 microns. Each particle/cluster contained bundles of nano-size HAP crystals (Figure 3.2). Type B (HAP) particles presented with similar morphology as Type C (Figure 3.3), however the average particle size was slightly larger. Type C (HAP) particles were generally spherical, with a wide range of particle size at micron level. Each particle had a rough outer surface (Figure 3.4).
Figure 3.1 SEM image of β-TCP filler
Figure 3.2 SEM image of the Hydroxyapatite Filler Type A
Figure 3.3 SEM image of the Hydroxyapatite Filler Type B
Figure 3.4 SEM image of the Hydroxyapatite Filler Type C
3.2 Particle Size Analysis

Figure 3.5 Particle size analysis results of β-TCP

Figure 3.6 Particle size analysis of Type A (HAP)
Figure 3.7 Particle size analysis of Type B (HAP)

Figure 3.8 Particle size analysis results of Type C (HAP)
The results of particle size analysis are summarized in Table 3.1

Table 3.1 Particle size analysis results of Fillers

<table>
<thead>
<tr>
<th>Fillers</th>
<th>&lt;10%</th>
<th>&lt;50%</th>
<th>&lt;90%</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-TCP</td>
<td>0.6µm</td>
<td>9.5µm</td>
<td>36.8µm</td>
</tr>
<tr>
<td>HAP (Type A)</td>
<td>0.8µm</td>
<td>3.9µm</td>
<td>16.4µm</td>
</tr>
<tr>
<td>HAP (Type B)</td>
<td>0.5µm</td>
<td>3.8µm</td>
<td>14.3µm</td>
</tr>
<tr>
<td>HAP (Type C)</td>
<td>1.5µm</td>
<td>11.3µm</td>
<td>29.9µm</td>
</tr>
</tbody>
</table>

3.3 **Vickers Micro Hardness**

3.3.1 **Hardness of Resin Composite containing β-TCP Filler**

Table 3.2 Vickers Micro hardness of the experimental resin composites containing β-TCP filler

<table>
<thead>
<tr>
<th>HAP Filler Loading (C73-13)</th>
<th>Vickers Micro hardness VHN (SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Immediately after curing</td>
</tr>
<tr>
<td>wt./wt % v/v %</td>
<td>wt./wt %</td>
</tr>
<tr>
<td>20</td>
<td>9.3</td>
</tr>
<tr>
<td>30</td>
<td>13.0</td>
</tr>
<tr>
<td>40</td>
<td>22.6</td>
</tr>
<tr>
<td>50</td>
<td>37.8</td>
</tr>
<tr>
<td>60</td>
<td>51.6</td>
</tr>
</tbody>
</table>

Differences between different filler loading ratios were indicated by different superscript letters (p<0.05).
3.3.2 Hardness of Resin Composite containing Type A (HAP) Filler

Table 3.3 Vickers Micro hardness of experimental resin composites (Type A)

<table>
<thead>
<tr>
<th>Filler loading (C13-09)</th>
<th>Vickers Micro hardness VHN (SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Immediately after curing</td>
</tr>
<tr>
<td>wt/wt %</td>
<td>v/v %</td>
</tr>
<tr>
<td>20</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Differences between different Hydroxyapatite loading types were indicated by different superscript letters (p<0.05).
3.3.3 Hardness of Resin Composite containing Type B (HAP) Filler

Table 3.4 Vickers Micro hardness of experimental resin composites (Type B)

<table>
<thead>
<tr>
<th>Filler Loading</th>
<th>Vickers Micro hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C73-08)</td>
<td>VHN (SD)</td>
</tr>
<tr>
<td>wt/wt</td>
<td>wt/v/v %</td>
</tr>
<tr>
<td>20</td>
<td>13</td>
</tr>
<tr>
<td>30</td>
<td>22</td>
</tr>
<tr>
<td>40</td>
<td>33</td>
</tr>
<tr>
<td>50</td>
<td>41</td>
</tr>
<tr>
<td>60</td>
<td>50</td>
</tr>
</tbody>
</table>

Differences between different Hydroxyapatite loading types were indicated by different superscript letters (p<0.05).
Figure 3.11 Vickers Micro hardness as a function of filler loading by volume (Type B)

3.3.4 Hardness of Resin Composite containing Type C (HAP) Filler

Table 3.5 Vickers Micro hardness of experimental resin composites (Type C)

<table>
<thead>
<tr>
<th>Filler loading (Ossea Cafosa)</th>
<th>Vickers Micro hardness VHN (SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt/wt %</td>
<td>Immediately after curing</td>
</tr>
<tr>
<td>20</td>
<td>10.6 (0.3)</td>
</tr>
<tr>
<td>30</td>
<td>12.1 (0.6)</td>
</tr>
<tr>
<td>40</td>
<td>16.2 (1.0)</td>
</tr>
<tr>
<td>50</td>
<td>13.7 (0.4)</td>
</tr>
<tr>
<td>60</td>
<td>11.3 (0.6)</td>
</tr>
<tr>
<td>v/v %</td>
<td>24 h after curing</td>
</tr>
<tr>
<td>20</td>
<td>18.6 (0.7)</td>
</tr>
<tr>
<td>30</td>
<td>21.6 (2.0)</td>
</tr>
<tr>
<td>40</td>
<td>25.0 (1.6)</td>
</tr>
<tr>
<td>50</td>
<td>25.3 (2.3)</td>
</tr>
<tr>
<td>60</td>
<td>21.1 (2.2)</td>
</tr>
</tbody>
</table>

Differences between different Hydroxyapatite loading types were indicated by different superscript letters (p<0.05).
3.3.5 Comparison of Trends between VHN vs Filler Load

The mean and standard deviations of Vickers Micro hardness values of the four resin composites types are presented in Tables 3.2 to 3.6. The VHN values of composites containing β-TCP ranged from 6.7 to 18.8 immediately after curing and from 19.5 to 33.5 after 24 h dry storage at 37 °C (Table 3.2). Pair wise multiple comparisons with Tukey’s post hoc test indicated significantly higher VHN values at higher filler loading. Regression analysis confirmed a positive correlation between filler loading and VHN (Figure 3.9).

The VHN values of β- TCP containing resin composites immediately after curing ranged from 12.1 to 16.8 and from 20.4 to 25 at 24h after curing as the filler ratio increased from 20% to 40 % (by weight). The VHN values decreased from 14.3 to 12.1 immediately after curing and from 21 to 19.9 after 24h at the filler loading ratios of 50% and 60% by weight respectively. The correlation between filler ratio and the VHN values for Type A immediately after curing is presented in Figure 3.10.

For Type B, the VHN values ranged between 11.8 to 15.1 immediately after curing and 19.7 to 23.5 at 24h after curing as the filler content increased from 20 to 50% (by weight). The VHN values were reduced to 14.8 immediately after curing and to 23 at 24h after curing as the filler content reached 60% by weight. The correlation between filler loading and the VHN values within Type B immediately and at 24 h after curing ($r^2= 0.99$ and 0.92 respectively) is
presented in Figure 3.11. The VHN values for Type C increased from 10.6 to 16.2 immediately after curing and from 18 to 25 at 24h after curing as the filler ratio increased from 20 to 40% by weight. However, the VHN values were reduced from 13.7 to 11.3 immediately after curing and from 25.3 and 21.1 at 24 h after curing at the filler ratios of 50% and 60% by weight respectively. The correlation between filler loading and the VHN values for Type C immediately after curing (r² = 0.83 respectively) and also at 24 h after curing (r² = 0.88) is presented in Figure 3.12.

3.4 Surface Gloss

3.4.1 Surface Gloss of Resin Composite containing β-TCP Filler

Table 3.6 Surface Gloss of experimental resin composites containing β-TCP filler

<table>
<thead>
<tr>
<th>Filler loading (c73-13)</th>
<th>Surface Gloss</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt/wt %</td>
<td>v/v %</td>
<td>At baseline</td>
<td>After polishing</td>
</tr>
<tr>
<td>20</td>
<td>9.3</td>
<td></td>
<td>53.7(5.7)</td>
<td>46.7 (2.7)</td>
</tr>
<tr>
<td>30</td>
<td>13.0</td>
<td></td>
<td>41.4 (7.1)</td>
<td>31.9 (4.5)</td>
</tr>
<tr>
<td>40</td>
<td>22.6</td>
<td></td>
<td>31.5 (2.2)</td>
<td>25.9 (3.3)</td>
</tr>
<tr>
<td>50</td>
<td>37.8</td>
<td></td>
<td>25.5 (3.6)</td>
<td>21.5 (1.6)</td>
</tr>
<tr>
<td>60</td>
<td>51.6</td>
<td></td>
<td>22.9 (4.0)</td>
<td>18.4 (2.3)</td>
</tr>
</tbody>
</table>

Differences between different filler loading ratios were indicated by different superscript letters (p<0.05).
Figure 3.13 Surface Gloss as a function of filler loading by volume

### 3.4.2 Surface Gloss of Resin Composite containing Type A (HAP) Filler

Table 3.7 Surface Gloss values of experimental resin composites (Type A)

<table>
<thead>
<tr>
<th>Filler loading (c13-09)</th>
<th>Surface Gloss</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>At baseline</td>
</tr>
<tr>
<td></td>
<td>wt/wt %</td>
</tr>
<tr>
<td>20</td>
<td>14</td>
</tr>
<tr>
<td>30</td>
<td>20</td>
</tr>
<tr>
<td>40</td>
<td>32</td>
</tr>
<tr>
<td>50</td>
<td>38</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
</tr>
</tbody>
</table>

Differences between different Hydroxyapatite loading types were indicated by different superscript letters (p<0.05).
3.4.3 Surface Gloss of Resin Composite containing Type B (HAP) Fillers

Table 3.8 Surface Gloss values of experimental resin composites (Type B)

<table>
<thead>
<tr>
<th>Filler loading (c73-08)</th>
<th>Surface Gloss</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>At baseline</td>
</tr>
<tr>
<td>wt/wt %</td>
<td>v/v%</td>
</tr>
<tr>
<td>20</td>
<td>13</td>
</tr>
<tr>
<td>30</td>
<td>22</td>
</tr>
<tr>
<td>40</td>
<td>33</td>
</tr>
<tr>
<td>50</td>
<td>41</td>
</tr>
<tr>
<td>60</td>
<td>50</td>
</tr>
</tbody>
</table>

Differences between different Hydroxyapatite loading types were indicated by different superscript letters (p<0.05).
Figure 3.15 Surface Gloss as a function of filler loading by volume (Type B)

3.4.4 Surface Gloss of Resin Composite containing HAP Type C Filler

Table 3.9 Surface Gloss values of experimental resin composites (Type C)

<table>
<thead>
<tr>
<th>Filler loading (ossea cafosa)</th>
<th>Surface Gloss</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>At baseline</td>
</tr>
<tr>
<td>wt/wt % v/v %</td>
<td></td>
</tr>
<tr>
<td>20 12</td>
<td>48.7(6.01)c</td>
</tr>
<tr>
<td>30 19</td>
<td>36.2(5.53)b</td>
</tr>
<tr>
<td>40 27</td>
<td>30.5(8.25)b</td>
</tr>
<tr>
<td>50 31</td>
<td>23.7(4.93)a</td>
</tr>
<tr>
<td>60 33</td>
<td>20.6(4.24)a</td>
</tr>
</tbody>
</table>

Differences between different Hydroxyapatite loading types were indicated by different superscript letters (p<0.05).
3.4.5 Comparison of Trends between Surface Gloss Vs Filler Load

The mean and standard deviation of all the four types of the experimental resin composites are presented in Tables 3.7 to 3.10.

The surface gloss values of β TCP containing resin composites at baseline decreased from 53.7 to 22.9, from 46.7 to 18.4 after polishing and from 32.9 to 19.6 after toothbrush abrasion as the filler content increased from 20 to 60 % (wt/wt %) respectively. One-way Anova indicated that there was a statistically significant (p < 0.05) between filler loading and surface gloss values at baseline, after polishing and after toothbrush abrasion. T-test for paired data indicated that polishing and toothbrush abrasion had a significant effect on the surface gloss values (p<0.05).

The average surface gloss values for β-TCP containing resin composites are presented in Table 3.6. The correlation between surface gloss and filler loading (v/v %) is presented in Figure 3.13.

The surface gloss values of Type A (HAP) fillers containing resin composites decreased from 58.3 to 39.5 at baseline, from 42.7 to 27.5 after polishing and from 26.7 to 19.6 after toothbrush abrasion as the filler ratio increased from 20 to 60 % (wt/wt %). One-way Anova indicated that there was a statistically significant interaction (p < 0.05) between filler loading and surface gloss values at baseline, after polishing and after toothbrush abrasion.
abrasion. T-test for paired data indicated that polishing and toothbrush abrasion had a significant effect on the surface gloss values (p<0.05). The average surface gloss values for Type A are presented Table 3.7. The correlation between surface gloss and filler loading (v/v %) is presented in Figure 3.14.

For Type B (HAP) composites, the surface gloss values reduced from 54 to 29.7 at baseline, from 38.12 to 29.2 after polishing and from 28.7 to 18.8 after toothbrush abrasion as the filler content increased. One-way Anova indicated that there was a statistically significant (p < 0.05) interaction between filler loading and surface gloss values at baseline, after polishing and after toothbrush abrasion. T-test for paired data indicated that polishing and toothbrush abrasion had a significant effect on the surface gloss values (p<0.05). The average surface gloss values for Type B are presented in Table 3.8. The correlation between surface gloss and filler loading (v/v %) is presented in Figure 3.15.

The surface gloss values for Type C (HAP) at baselines reduced from 48.7 to 20.6, from 25.7 to 17.7 after polishing and from 20.3 to 18.2 after toothbrush abrasion as the filler content increased. One-way Anova indicated that there was a statistically significant interaction (p<0.05) between filler loading and surface gloss values at baseline, after polishing and after toothbrush abrasion within all the four types. T-test for paired data indicated that polishing and toothbrush abrasion had a significant effect on the surface gloss values (p<0.05). The average surface gloss values for Type C are presented in Table 3.9. The correlation between surface gloss and filler loading (v/v%) is presented in Figure 3.16.
3.5 Surface Roughness

3.5.1 Surface Roughness of Resin Composite containing β-TCP Fillers

Table 3.10 Surface roughness of the experimental resin composites

<table>
<thead>
<tr>
<th>Filler loading</th>
<th>Wt/wt %, v/v %</th>
<th>At baseline</th>
<th>After polishing</th>
<th>After toothbrush abrasion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ra (µm)</td>
<td>Rt(µm)</td>
<td>Ra(µm)</td>
</tr>
<tr>
<td>20</td>
<td>9.3</td>
<td>0.28(0.06)a</td>
<td>3.7(1.32)c</td>
<td>0.46(0.06)d</td>
</tr>
<tr>
<td>30</td>
<td>13</td>
<td>0.26(0.08)a</td>
<td>3.8(0.97)b,c</td>
<td>0.31(0.03)b</td>
</tr>
<tr>
<td>40</td>
<td>22.6</td>
<td>0.24(0.11)a</td>
<td>3.77(1.17)b</td>
<td>0.30(0.04)b</td>
</tr>
<tr>
<td>50</td>
<td>37.8</td>
<td>0.24(0.08)a</td>
<td>3.17(0.45)b</td>
<td>0.23(0.9)b</td>
</tr>
<tr>
<td>60</td>
<td>51.6</td>
<td>0.29(0.08)a</td>
<td>3.64(0.32)a</td>
<td>0.28(0.08)a</td>
</tr>
</tbody>
</table>

Differences between different filler loading ratios were indicated by different superscript letters.

Differences between different filler loading ratios were indicated by different superscript letters.
Figure 3.17 Surface roughness parameters (a) Ra (b) Rt as a function of filler loading by volume

3.5.2 Surface Roughness of Resin Composite containing Type A (HAP) Fillers

Table 3.11 Surface roughness of the experimental resin composites (Type A)

<table>
<thead>
<tr>
<th>Filler loading</th>
<th>At baseline</th>
<th>After polishing</th>
<th>After toothbrush abrasion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ra</td>
<td>Rt</td>
<td>Ra</td>
</tr>
<tr>
<td>wt/wt v/v</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 14</td>
<td>0.41(0.04)</td>
<td>5.19(0.70)</td>
<td>0.47(0.08)</td>
</tr>
<tr>
<td>30 20</td>
<td>0.42(0.08)</td>
<td>4.56(0.94)</td>
<td>0.53(0.15)</td>
</tr>
<tr>
<td>40 32</td>
<td>0.43(0.13)</td>
<td>4.32(1.33)</td>
<td>0.59(0.26)</td>
</tr>
<tr>
<td>50 38</td>
<td>0.56(0.09)</td>
<td>4.07(0.3)</td>
<td>0.61(0.19)</td>
</tr>
<tr>
<td>60 40</td>
<td>0.53(0.12)</td>
<td>5.33(0.47)</td>
<td>0.6(0.2)</td>
</tr>
</tbody>
</table>

Differences between different Hydroxyapatite loading types were indicated by different superscript letters (p<0.05).
Figure 3.18 Surface roughness (a) Ra (b) Rt as a function of filler loading by volume (Type A)
## 3.5.3 Surface Roughness of Resin Composite containing Type B (HAP) Fillers

Table 3.12 Surface roughness of the experimental resin composites (Type B)

<table>
<thead>
<tr>
<th>Filler loading wt/wt %</th>
<th>v/v %</th>
<th>At baseline</th>
<th>After polishing</th>
<th>After toothbrush abrasion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ra</td>
<td>Rt</td>
<td>Ra</td>
</tr>
<tr>
<td>20</td>
<td>13</td>
<td>0.49(0.08)</td>
<td>4.52(1.02)</td>
<td>0.53(0.1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.85(0.07)</td>
</tr>
<tr>
<td>30</td>
<td>22</td>
<td>0.45(0.13)</td>
<td>5.43(0.50)</td>
<td>0.56(0.18)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.81(0.19)</td>
</tr>
<tr>
<td></td>
<td>33</td>
<td>0.5(0.07)</td>
<td>5.27(0.77)</td>
<td>0.58(0.13)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.78(0.18)</td>
</tr>
<tr>
<td>50</td>
<td>41</td>
<td>0.57(0.18)</td>
<td>4.89(1.47)</td>
<td>0.61(0.09)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.84(0.21)</td>
</tr>
<tr>
<td>60</td>
<td>50</td>
<td>0.63(0.18)</td>
<td>4.54(1.15)</td>
<td>0.65(0.17)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.81(0.33)</td>
</tr>
</tbody>
</table>

Differences between different Hydroxyapatite loading types were indicated by different superscript letters (p<0.05).
Figure 3.19 Surface roughness (a) Ra (b) Rt as a function of filler loading by volume (Type B)

3.5.4 Surface Roughness of Resin Composite containing Type C (HAP) Fillers

Table 3.13 Surface roughness (Ra, Rt) of experimental resin composites (Type C)

<table>
<thead>
<tr>
<th>Filler loading wt/wt</th>
<th>v/v %</th>
<th>At baseline</th>
<th>After polishing</th>
<th>After toothbrush abrasion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ra</td>
<td>Rt</td>
<td>Ra</td>
</tr>
<tr>
<td>20</td>
<td>14</td>
<td>0.49(0.9)a</td>
<td>6.38(0.9)a</td>
<td>0.66(0.08)a</td>
</tr>
<tr>
<td>30</td>
<td>20</td>
<td>0.54(0.1)a</td>
<td>7.11(1.0)ab</td>
<td>0.68(0.12)a</td>
</tr>
<tr>
<td>40</td>
<td>32</td>
<td>0.92(0.2)b</td>
<td>7.17(0.9)ab</td>
<td>1.01(0.14)a</td>
</tr>
<tr>
<td>50</td>
<td>38</td>
<td>1.01(0.1)b</td>
<td>7.88(0.9)bc</td>
<td>1.21(0.04)b</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>1.03(0.1)b</td>
<td>8.49(0.8)c</td>
<td>1.29(0.02)b</td>
</tr>
</tbody>
</table>

Differences between different Hydroxyapatite loading types were indicated by different superscripts (p<0.05)
Figure 3.20 Surface roughness (a) $R_t$ (b) $R_a$ as a function of filler loading by volume (Type C)
3.5.5 Comparison of Trends between Surface Roughness Vs Filler Load

For composites containing β-TCP, the Ra values at baseline ranged from 0.28 to 0.29, after polishing the Ra values dropped from 0.46 to 0.28 and from 0.79 to 0.59 after toothbrush abrasion as the filler content increased. The Rt values ranged from 3.7 to 3.64 at baseline, after polishing the Rt values dropped from 4.62 to 2.64 and from 6.08 to 5.37 after toothbrush abrasion as the filler content increased. One-way Anova indicated that there was a statistically significant interaction (p < 0.05) between filler loading and surface roughness parameters Ra and Rt after polishing and after toothbrush abrasion. T-test for paired data indicated that polishing and toothbrush abrasion had a significant effect on the surface roughness parameters (p<0.05). The average values of Ra ad Rt are presented in Table 3.10. The correlation between surface gloss and filler loading (v/v %) is presented in Figure 3.17.

For resin composites containing Type A (HAP) fillers, the Ra values ranged from 0.43 to 0.51 at baseline, from 0.47 to 0.60 after polishing and from 0.84 to 0.73 after toothbrush abrasion as the filler content increased. The Rt values ranged from 5.19 to 5.33 at baseline, from 4.6 to 5.94 after polishing and from 6 to 6.75 after toothbrush abrasion as the filler content increased. One-way Anova indicated that interaction between filler loading and surface roughness values at baseline, after polishing and after toothbrush abrasion was not statistically significant(p> 0.05). T-test for paired data indicated that polishing and toothbrush abrasion had a significant effect on the surface roughness parameters (p<0.05). The average Ra ad Rt values for Type A are presented in Table 3.11. The correlation between surface gloss and filler loading (v/v %) is presented in Figure 3.18.

For Type B, the Ra values at baseline ranged from 0.49 to 0.63, from 0.53 to 1.65 after polishing and from 0.85 to 0.81 after toothbrush abrasion as the filler content increased. The Rt value ranged from 4.52 to 4.54, from 5.71 to 5.58 after polishing and from 5.43 to 6.27 after toothbrush abrasion as the filler content increased. One-way Anova indicated that the interaction between filler
loading and surface roughness values at baseline, after polishing and after toothbrush abrasion was not statistically significant (p > 0.05). T-test for paired data indicated that polishing and toothbrush abrasion had a significant effect (p < 0.05) on the surface roughness parameters. The average Ra ad Rt values for Type B are presented in Table 3.12. The correlation between surface gloss and filler loading (v/v %) is presented in Figure 3.19.

For Type C, the Ra values ranged from 0.49 to 1.03, from 0.66 to 1.29 after polishing and from 0.81 to 1.37 after toothbrush abrasion as the filler content increased. The Rt values ranged from 6.38 to 8.49, from 6.89 to 8.30 after polishing and from 7.43 to 8.34 after toothbrush abrasion. One-way Anova indicated that there was a statistically significant (p < 0.05) interaction between filler loading and surface roughness parameters at baseline, after polishing and after toothbrush abrasion. T-test for paired data indicated that polishing and toothbrush abrasion had a significant effect (p < 0.05) on the surface roughness parameters. The average Ra ad Rt values for Type C are presented in Table 3.13. The correlation between surface gloss and filler loading (v/v %) is presented in Figure 3.20.
4 Discussion
4.1 Structure of Fillers

In the present study, the morphology of the filler particles was studied under a scanning electron microscope (FEI Inspect F, Oxford Instruments, UK). The SEM analysis showed that β-TCP and the hydroxyapatite fillers presented with significantly different morphologies as described in section 3.1. The SEM analysis demonstrated β-TCP fillers consisting of nano rods having a diameter of several hundred nanometers. The particle size analysis indicated that the average diameter was 9.5 µm as described in Table 3.1 However, it must be noted that in particle size analysis, the data is analyzed for anisodiametric (non-spherical) particles as if the particles were spheres. Therefore, the average diameters for β-TCP used in this study are for the equivalent spherical diameters.

4.2 Vickers Micro hardness

In the present study, the Vickers micro hardness test was used to measure the surface hardness of the resin composites. This method is commonly used to compare the surface hardness of dental composites. Vickers micro hardness was measured on the top surface of the specimens. Since the irradiance is reduced through the bulk of the resin composite due to light scattering, the top surface was selected for this study.

The primary variable within each type was filler loading. The VHN value for each type was measured immediately and at 24h after curing. It was observed that the VHN values of β TCP containing resin composites increased linearly ($r^2=0.99$) as the filler content increased from 20 to 60% (wt./wt. %). Thus the null hypothesis was rejected

However, the VHN values of Types A, B and C reached a threshold value and then remained constant or started to decline as the filler content increased. These results are in agreement with previous studies on HAP containing resin composites which suggest that hardness increased with increasing HAP compared to the unfilled resins as control and then start to decline [67, 96, and 99].

Furthermore, the resin composites containing β TCP demonstrated the highest VHN values as compared to the other three types. The possible explanation for relatively higher VHN values could be that the filler rods interlock and reinforce the matrix as
compared to the spherical HAP particles in other types. Moreover, the high aspect ratio increased the contact area between the filler and the matrix, thus enhancing the interfacial combination and surface hardness [96].

The secondary variable in the present study was post-irradiation time. There was a significant difference (p<0.05) in the VHN values for all the types immediately and after dry storage at 37ºC for 24 h. Thus the null hypothesis was rejected. These findings are in agreement with the previous studies which suggest that hardness increases steadily with time due to the progressive cross-linking reaction after the cessation of light-activation [102].

4.2.1 Comparison of Surface Hardness with Conventional Resin Composites

Previous studies have reported that the average VHN value of the unfilled resin is about 18. The VHN values of a heavily filled conventional microhybrid approaches 100 whereas the average VHN values of the conventional micro filled resin composite ranges from 30 to 40 [103]. The VHN values of the experimental types in this study were relatively lower than the commonly used conventional microhybrid resin composites. However, it must be noted that the filler volume fraction in the experimental resin composites was < 60% and thus they can be classified as a midway filled resin composites. Whereas the conventional microfilled composites are composed of 80-90% filler (wt./wt. %) [113]. Therefore, it can be assumed that for composites containing β-TCP, higher VHN values can be obtained by further increasing the filler content.

Furthermore, previous studies suggest that surface hardness can be improved by homogenous dispersion of the filler particles in the organic matrix. Stronger interactions between the filler and the organic matrix can improve the surface hardness. The chemical bonding at filler-resin matrix phase and the homogenous dispersion of the fillers can be improved by silane coupling agents [27, 99]. According to previous studies, the silanisation of the fillers significantly improves the Vickers hardness and mechanical strength of the resin composite [99]. The fillers used in the study can be surface treated with silane coupling agents to study the effect on surface hardness.
4.3 Surface Gloss

The optical properties of the resin composites are dependent upon factors such as filler morphology, filler content, dispersion of filler in the matrix and the differences in the refractive index between the resin matrix and the filler [104-106].

In this study, the surface gloss of the experimental resin composites was measured using a glossmeter. As the surface gloss depends upon the angle of light illumination and the angle of observer [107], a standardised gloss meter with 60° angle of illumination was used for all the specimens.

4.3.1 Surface Gloss after Curing

It was observed that the surface gloss values for all the resin composites reduced significantly (p<0.05) as the filler content increased. The highest gloss values were obtained after curing against a polyester strip. This is due to the presence of a highly glossy resin-rich layer over the surface.

As discussed earlier, the surface gloss of the materials is influenced by the filler morphology and the homogeneity of the filler-matrix complex. Larger filler size and lower dispersion of the filler particles in the resin matrix results in less light reflectivity and hence lower gloss values. Among the various types studied, resin composites containing Type C HAP possesses lowest gloss values as compared to the other three types. This could be explained by the fact that it consists of large irregular particle at micron level resulting in higher scattering as compared to the other three types.

4.3.2 Surface Gloss after Finishing and Polishing

The surface gloss after polishing is a function of their composition as well as the polishing method used [11]. In the present study, a series of aluminium-oxide multi-step finishing and polishing discs were used for all the specimens. To replicate a clinical situation, the polishing procedure was undertaken with hand piece and sequential disks, although this might potentially lead to variation in gloss measurements. The same finishing and polishing system was used for all the types to
ensure that only the differences between the materials compositions should be responsible for the different surface gloss values. It was observed that surface gloss values of the finished and polished were significantly reduced (p<0.05) as compared to baseline. The observed reduction could be attributed to the removal of the resin rich layer by finishing and polishing. As explained in section 1.7.6, the removal of the outermost composite by finishing/polishing procedures is necessary to produce a wear-resistant, harder, and colour stabilized restoration.

As discussed in section 4.3.1, the surface gloss and filler loading correlated negatively, a similar trend was observed after finishing and polishing. The finishing and polishing procedure resulted in the abrasion of the resin matrix, leaving the filler phase exposed [107]. Hence, surface gloss was more related to the characteristics of the filler exposed after finishing and polishing.

4.3.3 Surface Gloss after Toothbrush Abrasion

For all the materials tested, the surface became statistically less glossy (p <0.05) after toothbrush abrasion. As observed in the gloss values at baseline and after polishing, a clear trend could be seen where an increase in filler size led to reduction in gloss after toothbrush abrasion. In accordance with the present results, previous studies have demonstrated that abrasion of the softer resin results in the degradation of the resin matrix or weakening of resin-filler bond. As a result, there is a lack of support for the filler particles and they are pulled out from the surface. This leads to a roughening of the surface and the degree of random reflection of light increases resulting in the reduction of surface gloss values [66]. It must also be noted that all the experimental composites were composed of similar resin matrix system, so the difference in gloss values could be attributed to the differences in their filler component.

4.3.4 Comparison of Surface Gloss with Conventional Resin Composites

The surface gloss of the experimental resin composites was lower than most of the conventional resin composites. It must be noted that surface gloss of the resin composite depends on the difference in the refractive indices of the organic and inorganic phase [66]. The refractive index of the methacrylate resin matrix is between 1.5-1.55. In the conventional composites filled with quartz or glass, the refractive
indices of the fillers are in the range of 1.52-1.55. Hence, there is little or no
difference in the refractive indices between the organic and inorganic phase which
makes them appear translucent and glossy. Whereas, in the experimental resin
composites, fillers have a high refractive index (1.63-1.67) which makes them opaque
and less glossy [89]. However, it must be noted that the resin composites could be
opaque or translucent depends upon their use in different areas of dentition.

In addition, in the present study, surface gloss was reduced significantly after
polishing and after toothbrush abrasion. Gloss retention was strongly dependent on the
shape and mean particle size of the fillers. Previous studies demonstrate that nanofills
and microfills show reduced gloss after toothbrush abrasion while microhybrid
increase in gloss after toothbrush abrasion [11]

4.4 Surface Roughness

Surface roughness parameters are dependent on factors such as filler structure,
percentage of surface area occupied by filler particle, filler–resin matrix interaction
and the coupling agents [59, 60]. In this study, Ra and Rt values of the four different
types of resin composites series with variation in their filler size, morphology and
composition were measured after curing, polishing and after toothbrush abrasion.

Surface roughness can be measured by various methods including contact stylus
tracing, scanning electronic microscope, laser reflectivity and non-contact
confocal microscopy. In the present study, a 3-D non-contact stylus profilometer
was used which has the advantage of rapid quantitative measurement without
damaging the specimen.

Vertical roughness parameters Ra and Rt were used to describe the surface
roughness. The surface roughness parameter Ra is most commonly used to estimate
the surface quality of resin composite materials in amplitude.

4.4.1 Surface Roughness after Curing

The results of this study indicated that there was a significant interaction (p<
0.05) between filler loading and surface roughness parameters. The Ra and Rt
values increased as the filler contents increased.
β-TCP containing resin composites expressed the lowest Ra and Rt values among the materials investigated. Type A and B hydroxyapatite containing resin composites, which possess relatively similar chemical composition and filler morphology presented with comparable Ra and R-values. Whereas, Type C resin composites which consists of relatively larger micro sized irregular particles presented with highest Ra and Rt values. Ra and Rt values in this study were not only affected by the particle size, but also by the shape of filler particles [52]. These results are consistent with those of other studies and suggest that the surface roughness values increased with the increase of filler particle size and also with irregular shaped fillers [55].

4.4.2 Surface Roughness after Finishing and Polishing

In the present study, the surface roughness values of all the resin composites increased after finishing and polishing. It has been demonstrated by previous studies that finishing and polishing results in removal of the softer organic matrix. This results in projection of the unsupported filler particles and the surface of the resin composite become more or less deformed which increases the surface roughness [107]. However, the results of this study varied significantly among the four filler types. For β-TCP containing resin composites, the Ra values dropped from 0.46 to 0.18 µm and Rt from 4.26 to 2.64 as the filler content increased from 20 to 60% (wt/wt %). These findings can be explained in accordance with the previous studies which suggest that reduced inter particle spacing at higher filler loading improves the wear resistance of the resin composite [63] and [64, 108, 109]. Also, the inter particle spacing is reduced in finer particles as they can be closely packed together as compared to the larger filler particles. It is possible, therefore that the finer filler particles of β-TCP were closer together in the resin matrix and protected the resin from abrasives thus improving the wear resistance and surface quality after polishing. [62]. However, more studies need to be undertaken before the association between the filler structure and the Ra, Rt values after polishing wear for this particular type of fillers is clearly understood.

For types A and B (HAP) containing resin composites, no such interaction between filler loading and surface roughness was observed as the Ra and Rt values did not change significantly with variations in filler loading. Type C (HAP) presented with the
highest surface roughness values among the four types. The Ra values increased from 1.66 to 1.29 and the Rt values from 6.89 to 8.30 as the filler content increased from 20 to 60% (wt/wt %) respectively. As explained above, the finishing and polishing procedure removed the resin matrix and the rougher irregular filler particles protruded from the surface resulting in higher Ra and Rt values.

It must be mentioned that the surface quality of a resin composite restoration after polishing depends on the composition of the resin composite as well as the polishing system used [107, 110]. However, in the present study, a single polishing system was used for all the resin composites as the aim was to correlate the structure with the surface properties and not to compare the different polishing methods.

4.4.3 Surface Roughness after Toothbrush Abrasion

Toothbrush abrasion increased the roughness parameters Ra, Rt significantly (p<0.05) for all the resin composite types. For resin composites containing β-TCP, a trend similar to the one observed after polishing was observed. Ra and Rt values decreased as the filler content increased. For types A and B (HAP) containing resin composites, Ra and Rt did not change significantly as the filler content was raised.

However, the Ra values for Type C increased significantly (p<0.05) with the increase in filler content. The differences in the surface roughness parameters among the four types could be explained by variations in their structure.

The β-TCP fillers particles consists of higher filler volume fraction as compared to the HAP containing resin composites. The higher volume fraction resulted in smaller distance between the neighboring particles resulting in improved wear resistance and reduced surface roughness after toothbrush abrasion.

The filler particles in resin composites containing HAP Types A and B possess similar micro structure, presented with comparable Ra and Rt values. For Type C (HAP), the Ra and Rt values after toothbrush abrasion increased significantly as the filler content was increased. Moreover, Type C exhibited highest Ra and Rt values among the four types. Type C filler particles were rough irregular particles as indicated by the SEM analysis. It has been demonstrated by previous studies that toothbrush abrasion results in stress concentration around the filler particles which causes pull-out of the irregular particles from the surface explaining the high surface roughness values. [109].
4.4.4 Comparison of Surface Roughness with the Conventional Resin Composites

Previous studies have suggested that the Ra values should be similar to the biologically smooth enamel-to-enamel occlusal contact possessing a Ra value of 0.64 ± 0.25 mm [111]. The critical threshold Ra value for bacterial adhesion is 0.2 μm. Ra values higher than 0.2 μm result in increased plaque accumulation and pose a higher risk for dental caries and periodontal diseases [112]. In the present study, resin composites containing β-TCP had Ra value less than the threshold value. However, for resin composites containing HAP fillers, surface roughness (Ra) values exceeded the clinically acceptable threshold for restorations.

In addition, previous studies on resin composites have reported a strong correlation between surface gloss and surface roughness [76, 113]. When surface roughness increases, the degree of random reflection of light increases, ultimately resulting in reduced gloss [114]. This correlation between surface gloss and surface roughness was observed only for Type C. Therefore, it can be assumed that other factors such as morphology of the filler particles influenced the surface gloss and surface roughness relationship in the experimental resin composites.

4.5 Conclusions

4.5.1 Surface Hardness

1. In terms of surface hardness, β-TCP containing resin composites presented with highest VHN value which was directly correlated with the filler content.
2. The VHN values of composites containing fillers with identical morphology presented with comparable VHN values and followed a similar trend as the filler content was raised. The VHN values of resin composites with micro sized HAP fillers increased and then reached a threshold and either remained static or started to decline with an increase in filler content.

4.5.2 Surface Gloss

1. The surface gloss values declined as the filler content increased for all the resin
composites.

2. The resin composites containing β-TCP fillers, presented with highest gloss values as compared to the other three types.

3. The HAP fillers with identical morphology and particle size presented with comparable gloss values.

4. The HAP fillers consisting of relatively larger, rough particles presented with lowest gloss values.

4.5.3 Surface Roughness

1. The resin composites containing β-TCP particles presented with lowest Ra and Rt values. The roughness values decreased as the filler content was increased after polishing and toothbrush abrasion.

2. Ra and Rt values did not change significantly as the filler content was increased for the resin composites consisting of micro sized HAP spherical particles.

3. Ra and Rt values of the resin composites with rough micro sized HAP particles increased significantly as the filler content was increased. They presented with highest roughness values at baseline, after polishing and after toothbrush abrasion.
5 General Discussion
and
Future Recommendations
5.1 General Discussion

The results obtained showed that the filler content, particle size and structure are the key factors, which modify significantly the final properties of the resin composite, and that specially affects the acceptance and longevity of the resin restoration. Therefore, these are the parameters that can be very useful in order to adjust the behavior of the resin composite to the specific clinical requirements. Within the limitations of this study, it can be concluded that properties vary in a complex manner with variations in the structure and content of the filler phase particle.

In the present study, resin composites containing β-TCP fillers, presented with higher surface hardness and surface gloss and relatively lower surface roughness values. Among the HAP containing resin composites, Types A and B spherical particles demonstrated higher surface gloss and lower surface roughness values as compared to Type C irregular particles whereas their surface hardness results were almost identical. Hence within the limitations of this study, on the basis of the properties investigated in this study, it can be concluded that among the various fillers studied, β-TCP could be a promising filler to fabricate bioactive resin composites.

5.2 Future Recommendations

Further research is needed to study other important properties such as radiopacity, degree of conversion and polymerization shrinkage. The remineralisation potential of the resin composites prepared in the present study should also be investigated. For research purposes, the fillers could be surface treated with coupling agent and their key properties could be compared with the resin composites used in this study.

Furthermore, as already discussed in the introduction section, β-TCP converts to HAP under aqueous conditions. However, this finding was not investigated in this study and will be extremely interesting as future work.
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